ON THE CHEMICAL CONSTITUTION OF CLUPANODONIC ACID.

By **Mitsumaru TSUJIMOTO.**

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The unsaturated acids occurring in natural oils and fats, which have hitherto been investigated by chemists for their chemical constitution, are chiefly those of the oleic acid series. Of the acids of higher unsaturation we may count only linolic, elaeostearic, and linolenic acids. As to the so-called highly unsaturated acids ($C_nH_{2n-8}O_2$ and $C_nH_{2n-10}O_2$ series), which occur commonly and abundantly in marine animal oils, no reliable investigation has yet been performed, and at present we lack nearly wholly the definite knowledge of their constitution. The present paper deals with the constitution of clupanodonic acid, $C_{22}H_{34}O_2$, which is one of the most important and typical members of such series.

More than thirty years ago W. Fahrion[1] reported that on oxidising "jecoric acid", $C_{18}H_{30}O_2$, by Hazura's oxidation method he was unable to obtain hydroxylated acids, except volatile acids and carbon dioxide. Presumably his "jecoric acid" was impure highly unsaturated acids. R. Majima and T. Okada[2] attempted to investigate the constitution of clupanodonic acid, but the acid obtained by debrominating the polybromide of the fatty acids of Japanese sardine oil was found not to be a simple chemical compound; so they were obliged to gave up their original project. Recently from a study on the fatty acids of a "South Georgia whale oil", E. F. Armstrong and T. P. Hilditch[3] made an interesting statement that in C_{20} and C_{22} acid groups was there slightest evidence of the occurrence of an ethylenic linkage between the carboxyl group and the ninth carbon atom in the chain. This conclusion appears, however, to be too hasty, inasmuch as they did not isolated the C_{20} and C_{22} highly unsaturated acids, but oxidised the mixed acid fractions respectively. But there must have been present a large amount of less unsaturated acids, such as $C_{20}H_{38}O_2$ (gadoleic acid ?) and cetoleic acid, $C_{22}H_{42}O_2$, in the fractions, whereas the amount of the highly unsaturated acids was small.[4] The statement propounded by R. R. Mc Gregor with G. D. Beal[5] on the limit of unsaturation in menhaden oil is

(1) *Chem. Ztg.*, **17** (1893), 521.
(2) *J. Tokyo Chem. Soc.*, **35** (1914), 13.
(3) *J. Soc. Chem. Ind.*, **44** (1925), 180 T.
(4) Y. Toyama, *Chem. Umschau*, **31** (1924), 221, 238; **33** (1926), 293; **34** (1927), 19.
(5) *J. Am. Chem. Soc.*, **48** (1926), 3150.

essentially an amplification of the conclusion of Armstrong and Hilditch. Nor were they able to arrive at definite results by the decomposition of the ozonides of the highly unsaturated acids.

The present writer has succeeded to isolate nearly pure clupanodonic acid by his lithium-salt-acetone method.[1] The method of bromination and debromination hitherto used for the isolation of polyethylenic acids, such as linolic and linolenic acids, has a drawback that there is no certain proof that the position of ethylenic linkage is not displaced by such violent chemical treatments. The comparatively mild treatments (saponification, esterification, distillation under diminished pressure) of the writer's method are probably free from the above defect.

Clupanodonic acid readily absorbs ozone in chloroformic solution forming ozonide. But this compound appears to be unstable and it has been found difficult to obtain it in pure state. On decomposing the ozonide with water, the nearly whole part of the decomposition products go to the solution leaving only a small amount of an oily insoluble substance. By the writer's experiments, there were found as volatile decomposition products acetaldehyde, propionaldehyde, and carbon dioxide, and as non-volatile product a comparatively large amount of succinic acid. Azelaic acid and other higher dibasic acids, or their semialdehydes were found not to be present, at least appreciably. According to Armstrong and Hilditch's statement, a marked amount of such compounds should be present in the decomposition products.

As the decomposition products of clupanodonic acid ozonide were mainly soluble in water, so for the confirmation of the product containing the carboxyl group, the amyl ester of the acid was ozonised and decomposed with water. By this means an insoluble decomposition product containing the esterified carboxyl group was obtained, which on saponification yielded succinic acid. So the product contained four carbon atoms; therefore the first ethylenic linkage in clupanodonic acid is situated between fourth and fifth carbon atoms counting from the carboxyl group. Acetaldehyde and carbon dioxide were likely formed as the secondary decomposition products of malonic dialdehyde, or semialdehyde of malonic acid. Now calculating from the amount of the carbon dioxide formed, the atomic group, $=CH{\cdot}CH_2{\cdot}CH=$, contained in a molecule of clupanodonic acid is probably one. Conjugate double bonds are probably not present, since neither glyoxal nor glyoxylic acid was detected, and also no trace of oxalic acid was found; also by heating clupanodonic acid with metallic sodium and alcohol, no lowering of the iodine value was observed. The presence of triple bonds is negated by the fact that the iodine value of clupanodonic acid and the

(1) *Chem. Umschau*, **27** (1920), 229; **33** (1926), 285.

bromine content of its bromine addition compound closely agree with the numbers calculated from five double bonds.

By the above mentioned results, it has been confirmed that the molecule of clupanodonic acid consists of the following atomic groups: (1) $CH_3{\cdot}CH_2{\cdot}CH=$, (2) $=CH{\cdot}CH_2{\cdot}CH=$, (3) $=CH{\cdot}(CH_2)_2CH=$, and (4) $=CH{\cdot}(CH_2)_2{\cdot}COOH$. As to some of the arrangement of these groups, no definite data have yet been obtained. But according to a recent investigation of Y. Toyama,[1] cetoleic acid, $C_{22}H_{42}O_2$, which occurs widely distributed in marine animal oils and has 22 carbon atoms alike to clupanodonic acid, has been proved to be $\Delta^{11,12}$ dococenic acid. From the fact that linolic and linolenic acids have each an ethylenic linkage between ninth and tenth carbon atoms as oleic acid, so if we assume an analogy exists in the case of clupanodonic and cetoleic acids, it is not unreasonable to think that clupanodonic acid has an ethylenic linkage between eleventh and twelfth carbon atoms as cetoleic acid. Then the possible arrangement of carbon atoms in the molecule of clupanodonic acid is $C_3=C_4=C_4=C_4=C_3=C_4$ (right end—carboxyl) and $C_3=C_4=C_4=C_3=C_4=C_4$ (ibid.), so that the constitution of clupanodonic acid will be one of the following two formulae:[2]

(1) $CH_3{\cdot}CH_2{\cdot}CH:CH{\cdot}(CH_2)_2CH:CH\,(CH_2)_2{\cdot}CH:CH{\cdot}(CH_2)_2\,CH:CH{\cdot}CH_2{\cdot}CH:CH\,(CH_2)_2{\cdot}COOH$.

(2) $CH_3{\cdot}CH_2{\cdot}CH:CH\,(CH_2)_2\,CH:CH\,(CH_2)_2\,CH:CH{\cdot}CH_2{\cdot}CH:CH\,(CH_2)_2{\cdot}CH:CH{\cdot}(CH_2)_2\,COOH$.

As the decomposition products of clupanodonic acid ozonide are very complicated, no pretension can be insisted for not overlooking some important compounds. And as some of the arrangement of the atomic groups is hypothetical, the above formulae have only been proposed provisionally. Further investigations may verify or correct them. As to the arrangement of the atomic groups, the examination of the decomposition products of partially hydrogenated clupanodonic acid may probably furnish some clue for its definite confirmation.

Experimental Part.

(I) **Material.** The fatty acids of a Japanese sardine oil from Hokkaidō were treated by the lithium-salt-acetone method, and the highly unsaturated acids so obtained were changed to the methyl esters and fractionated under 5 mm. pressure. The fraction boiling at 217–226° was taken as the methyl ester of clupanodonic acid. It was saponified and the accompanying small

(1) *Chem. Umschau*, **35** (1928), 20.

(2) That clupanodonic acid has straight chain structure is already known by the formation of behenic acid on hydrogenation.

amount of unsaponifiable matter was removed, and finally oxidised acids were separated by means of petroleum ether. The clupanodonic acid thus refined had the following properties: $d_4^{15}=0\,9410$, neutralisation value 170.7, iodine value 388.8, $n_D^{15}=1.5057$. Calculated for $C_{22}H_{34}O_2$: neutr. value 169.8, iodine value 384.3.

The specific gravity and refractive index were respectively higher than those of previously obtained. Whether these are due to the presence of more highly unsaturated acids (e. g. $C_{22}H_{32}O_2$), or the previously isolated clupanodonic acid was still contaminated with less unsaturated acids, is not certain. In the present experiments the above sample was, however, accepted as pure clupanodonic acid.

(II) **Preparation of Clupanodonic Acid Ozonide.** Five gr. of clupanodonic acid were dissolved in 50 c.c. of chloroform, and on cooling with ice and salt a current of ozonised oxygen (washed with 5% NaOH solution and sulphuric acid; ozone content ca. 5%) was passed into the solution at the rate of 6 litres per hour during for 5 hours. Then the chloroform was distilled off under a diminished pressure at about 30°. By keeping the ozonide over night under diminished pressure it was decomposed with water. The yield of the ozonide was 11–12 gr. per 5 gr. of the acid, so that it was much higher than that calculated for normal ozonide (8.6 gr.). This was probably due to the difficulty of removing last part of the solvent. The ozonide appeared also to be unstable, so it was decomposed next day without further keeping.

The ozonide thus obtained formed a pale yellow, elastic, linoxyn-like mass, and burned explosively when heated. Great difficulty was experienced in its elementary analysis, and the result was very unsatisfactorily. The carbon content was found apparently much higher; this was probably caused by adhered chloroform.

(III) **Decomposition of Clupanodonic Acid Ozonide with Water.** To the ozonide obtained from 5 gr. of clupanodonic acid, 100 c.c. of water were added and heated on a water bath in the current of hydrogen. The flask was fitted with a condenser, and the latter in turn combined to the following three flasks, through which the evolved gas together with hydrogen may pass without leakage: (*a*) 50 c.c. of water (cooled with ice), (*b*) 150 c.c. of ca. N/3 $Ba(OH)_2$ solution, (*c*) 50 c.c. of the same. As the ozonide by rapid heating with water made an explosion-like decomposition, so the mixture was at first very carefully warmed to 65–70°, and kept somewhat long time at this temperature, and then the temperature was gradually raised till the water in the bath boiled. The ozonide decomposed with evolution of gas, firstly floated on the surface of water as a viscous oily liquid, this then gradually went to the solution, and finally there remained at the bottom of

the flask a small amount of a brownish insoluble liquid substance. The solution became discoloured by degrees and assumed a brownish orange-yellow colour. The above operation was five times repeated and so totally the ozonide obtained from 25 gr. of clupanodonic acid was decomposed.

(1) *Volatile Decomposition Products.* The volatile products caught in the flasks *a*, *b* and *c* were examined.

(*a*) The solution in the flask *a* showed marked aldehyde reactions. A colourless liquid collected at the bottom of the flask was found to be admixed chloroform. With *p*-nitrophenylhydrazine and hydrochloric acid the solution gave a bright orange-yellow precipitate, which on twice recrystallisations from 50% alcohol, formed orange-yellow needles of melting point 116.5–117°. 0.1138 gr. subst. gave 0.2308 gr. CO_2 and 0.0581 gr. H_2O; 0.1425 gr. subst. gave 28.9 c.c. nitrogen (23°, 756 mm.). (Found : C=55.31; H=5.71; N=22.61. $C_9H_9O_2N_3$ requires C=53.60; H=5.07; N=23.47. $C_9H_{11}O_2N_3$ requires C=55.93; H=5.74; N=21.76%). The percentage of carbon and hydrogen corresponded nearly to those of the nitrophenylhydrazone of propionaldehyde, but that of nitrogen was the mean of those of the compounds of acetaldehyde and propionaldehyde. The presence of the two aldehydes was proved by (1) diethylamine and sodium nitroprusside (acetaldehyde), and (2) skatole reaction (propionaldehyde).

(*b*) The precipitate formed in the flasks, *b* and *c*, appeared to consist of barium carbonate. The carbon dioxide was possibly formed as the secondary decomposition product of the ozonide. For its quantitative determination, the following procedure was adopted. The excess of $Ba(OH)_2$ was firstly neutralised with N/2 hydrochloric acid using phenolphthalein as indicator. Then adding methylorange as indicator the further addition of hydrochloric acid was made until the white precipitate was dissolved and the solution assumed a clear pink colour. From the amount of HCl used for the second titration, the weight of carbon dioxide was calculated.

The determination was repeated with the ozonide obtained from each 5 gr. of clupanodonic acid. As the most reliable number, the writer obtained 0.838 gr., i.e. ca. 16.8% for clupanodonic acid. The presence of acetaldehyde and carbon dioxide in the decomposition products of the ozonide is, as already stated, probably due to the secondary decomposition of malonic dialdehyde, or semialdehyde of malonic acid. So it may be inferred that in the molecule of clupanodonic acid there are contained atomic groups, such as $=CH\cdot CH_2\cdot CH=$ or $=CH\cdot CH_2\cdot COOH$. If there is only one such group, $=CH\cdot CH_2\cdot CH=$ (40) in one molecule of clupanodonic acid (330.3), then the carbon dioxide formed by the decomposition ($CH\cdot CH_2\cdot CH \rightarrow CO_2 + CH_3\cdot CHO$) must be 13.3% for clupanodonic acid. The number obtained above (16.8%) was somewhat greater than it, but if we assume the presence of two such

groups, then the amount of carbon dioxide is too small, so that the number of the group contained is probably only one. That the carboxyl is not contained in the group was confirmed by the experiments made on the ozonide of the amyl ester of clupanodonic acid (see below).

(2) *Non-Volatile Decomposition Products.* The aqueous solution of the decomposition products obtained from each 5 gr. of clupanodonic acid ozonide was treated as follows:

Firstly the solution was filtered through a filter paper, thereby the insoluble substance was left. The filtrate was twice treated with each 150 c.c. of ether, the ether layer separated from the lower aqueous solution (*C*), and treated with sodium bicarbonate solution in a separating funnel. The upper ether solution was separated, dehydrated with anhydrous magnesium sulphate and the ether distilled off. The thereby remaining portion (*A*) consisted chiefly of aldehydic constituents. The sodium bicarbonate extract was acidified with dilute hydrochloric acid and exhausted with ether (three times with each 100 c.c.) and then ether distilled off; by this operation the acidic constituents (*B*) were obtained. The yield of the products was found difficult to determine exactly, chiefly owing to their volatility. But roughly speaking the following numbers were obtained:

From the ozonide of 10 gr. of clupanodonic acid: *A* only 0.3 gr.; *B* 3.2 gr.; *C* or the aqueous solution separated from ether layer was evaporated under a diminished pressure, and about 5 gr. of the residue was obtained. On the evaporation the solution became discoloured, and a substance difficultly soluble in ether or water was produced. This was probably the resinified products of aldehydes. The insoluble oily substance firstly formed was about 0.6 gr.

(a) Part *A*. On distilling off the ether, an orange-yellow liquid was left. This was difficultly soluble in water; it formed with nitrophenylhydrazine a dark reddish viscous precipitate, and with semicarbazide hydrochloride a semicarbazone (?) of m.p. above 200°. As no definite derivative was obtained, the substance was analysed as follows: 0.1373 gr. subst. gave 0.3033 gr. CO_2 and 0.0946 gr. H_2O. (Found C=60.25, H=7.71%). If we consider the substance to be an aldehyde or its polymerised product, so succinic dialdehyde $C_4H_6O_2$ (C=55.78, H=7.03%) or glutaric dialdehyde $C_5H_8O_2$ (C=59.96, H=8.06%) correspond somewhat to it.

(b) Part *B*. From the ozonide of 25 gr. of clupanodonic acid, about 8 gr. of this part was obtained. It formed an orange-yellow liquid not solidified by cooling in ice. It was firstly distilled at the ordinary pressure, thereby at the bath temperature of 140° the distillation began. At the bath temperature of 160° (dist. temp. ca 110°) the distillation was interrupted. The distillate (*B*1) amounted to 1.9 gr.; a pale yellow pungent liquid of

$n_D^{20}=1.3700$ and of aldehydic reaction. Then the distillation was continued under 6 mm. pressure. Up to the bath temp. of 180° and the distillation temp. of 135°, 0.8 gr. of distillate (*B*2) was obtained; this was a pale orange-yellow liquid. By this temperature, the indication of decomposition was observed; so the distillation was stopped. The residue (*B*3), 4.2 gr.; a dark brown viscous liquid mixed with crystals.

*B*1. This was dissolved in alcohol and titrated with $Ba(OH)_2$ solution (acid value found was 520); it was then exhausted with ether to remove aldehydic compounds. The barium salt obtained by evaporating the alcohol and water contained 55.4%Ba, ($(C_2H_3O_2)_2Ba$ requires Ba=53.79%); so the acid seemed to consist of acetic acid. But judging from somewhat high distillation temperature, there appeared the presence of propionic acid (b.p. 141°) to be likely.

*B*2. Showed a marked aldehyde reaction and had the acid value 425. On oxidising it with alkaline potassium permanganate solution, white crystals were obtained. On carefully washing with ether, they melted at 177.5° and the mixed melting point test with succinic acid[1] showed 180–181°. So this substance was confirmed to be succinic acid. The crude product probably contained succinic semialdehyde.

*B*3. Showed also a marked aldehyde reaction. By treating it with ether, a brown tarry insoluble substance was left; it was, however, completely soluble in acetic ether. On oxidising it with alkaline potassium permanganate solution, a yellowish white crystalline semisolid was obtained with a yield of 70%; the white crystals obtained by treating it with ether to remove the liquid part melted at about 177° and the mixed test with succinic acid was 179–180°. So the substance was confirmed to be also succinic acid.

(c) Part *C*. On distilling off the ether under a diminished pressure, a dark brownish viscous substance was obtained. It was soluble in acetone and acetic ether, but on treatment with ether, a black-brown viscous substance was left. This was probably polymerised aldehydes. As the substance did not distil under diminished pressure when heated to a bath temperature of 150°, so the content of the flask was dissolved out with acetone (thereby much amount of tarry substance was separated). The substance left on evaporating off the acetone was dissolved in a little water and exhausted with ether. On evaporating off the ether, an extract was obtained with a yield of about 54%. This was a mixture of crystals and an orange-yellow liquid. It was then treated with cold ether to remove the liquid part, and the crystals were dissolved in acetic ether, and decolourised with animal charcoal. On concentration and cooling, the solution deposited white crystals,

(1) Merck, m. p. 183-183.5°. In this and in the following experiments, always equal parts were mixed.

which melted at 182–182.5° and had the neutralisation value 936. The mixed test with succinic acid was 182°. So the substance was succinic acid.

On directly oxidising the original substance with alkaline potassium permanganate solution, white crystals of m.p. 182–182.5° (mixed test with succinic acid 181.5–182°) and the neutr. value 934 were obtained. Its elementary analysis gave the following result: 0.1187 gr. subst. gave 0.1786 gr. CO_2 and 0.0574 gr. H_2O. (Found: C=41.04; H=5.41. $C_4H_6O_4$ requires C=40.66; H=5.12%). The substance was, therefore, confirmed to be succinic acid.

Beside the above mentioned experiments the insoluble oily substance, which was formed in a small amount on decomposing the ozonide with water, was oxidised, and a substance (white crystals) resembling azelaic acid was obtained, but owing to its small quantity it was found difficult to confirm it with certainty. If this was really azelaic acid, then the oily substance was probably formed from ozonides of some less unsaturated acids, which were contaminated in the sample of clupanodonic acid.

(IV) **Decomposition of the Amyl Ester Ozonide of Clupanodonic Acid.** This experiment was undertaken to confirm the position of the ethylenic linkage nearest to the carboxyl group. As the decomposition products of clupanodonic acid ozonide with water are nearly wholly soluble in water, in order to settle the question the writer has esterified the acid with a sparingly soluble alkyl group and ozonised it. By decomposition with water, the atomic group containing the esterified carboxyl group will be obtained as an insoluble product and its nature may be identified. Apparently a higher alkyl group would be better for the purpose, but as it is difficult to expel it, so amyl group was chosen for the experiment.

Six gr. of clupanodonic acid, 24 gr. of amyl alcohol containing 2.5% of HCl and 30 c.c. of ether were heated in a flask with a reflux condenser on a water bath in the current of carbon dioxide for one hour and then the content of the flask was washed with water, taken up with ether, and dried with anhydrous sodium sulphate. The ether was then distilled off and the excess of amyl alcohol was removed under a diminished pressure. The amyl ester so prepared had the acid value of 9.9 showing some presence of free acid, but as it had the saponification value 139.5, nearly corresponding to that (140.1) of amyl clupanodonate, $C_{21}H_{33}COOC_5H_{11}$, it was used as the material for ozonisation.

Five gr. of the amyl ester were dissolved in 50 c.c. of chloroform and ozonised. The yield of the ozonide, which contained still some amount of the solvent, was 9.8 gr. It was an orange-yellow viscous liquid. On heating it with 80 c.c. of water on a water bath for one hour, there was observed an appreciable amount of an orange-yellow insoluble oily liquid formed at the

bottom of the flask. The supernatant liquid was filtered off and the oily substance was again heated with 8 times of water in order to complete the decomposition. The oily substance finally left was 2.46 gr. corresponding to about 49% of the original ester.

This substance was dissolved in alcohol and titrated with alcoholic potash to neutralisation, and then on adding water the aldehydic or neutral substances were extracted with ether, and the aqueous solution was acidified with hydrochloric acid and exhausted with ether. On distilling off the ether, about 32% of a dark brownish liquid of the neutralisation value 255 was obtained (neutr. value of mono-amyl ester of succinic acid $HOOC(CH_2)_2 \cdot COOC_5H_{11} = 298.2$). Then the substance was saponified with an excess of alcoholic potash and acidifying with hydrochloric acid the free acid was extracted with ether. The extract consisted of a mixture of liquid and crystals. This was treated with ice-cooled ether to remove the liquid part and then the crystals were dissolved in acetic ether and decolourised with animal charcoal. On concentrating the solution and cooling with ice, crystals were obtained, which melted at 177° and had the neutralisation value 605. As this seemed still to contain some amount of neutral substances, so the neutralised solution was evaporated to dryness, dissolved in water and treated with ether. To the aqueous solution, dilute hydrochloric acid was added, and the free acid was exhausted with ether. The solid remaining on evaporating off the ether melted at 179–180° and had the neutr. value 944. The mixed test with succinic acid was 181–181.5°. So this substance was identified as succinic acid.

Then the firstly extracted aldehydic part (ca. 42%) was examined. It was oxidised with an alkaline potassium permanganate solution and the product was neutralised with alcoholic potash, and the neutral substances extracted with ether. From the lower aqueous solution on decomposing it with hydrochloric acid there was obtained by exhausting with ether a substance probably consisting of mono-amyl ester of succinic acid. It was a pale yellow liquid of the neutr. value 294. On saponification the free acid was obtained; it was refined by means of acetic ether. The substance formed white crystals of m.p. 180. The mixed test with succinic acid was 181–181.5; so this was also succinic acid.

From the above results it has been concluded that among the decomposition products of the ozonide of amyl clupanodonate, that part which is combined with the amyl group is succinic acid. Therefore the ethylenic linkage nearest to the carboxyl group in the molecule of clupanodonic acid is situated between fourth and fifth carbon atoms counting from the carboxyl group. The calculated percentage of succinic mono-amyl ester to be obtained from amyl clupanodonate is 47%. The yield of 49% nearly corresponded to it.

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AN INTERPRETATION OF THE REARRANGEMENTS OF PINACONES AND TERTIARY AMINO-ALCOHOLS FROM THE ELECTRON THEORY OF VALENCY (THEORETICAL PART).

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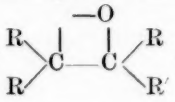
Introduction. Since the discovery of triphenyl-methyl by Gomberg, the theory of "Valenzbeanspruchung" has played an important rôle in the theoretical line of the organic chemistry. Consequently the comparison of firmness of attachment of organic radicals to an element affords one of the most interesting subjects. Thus, J. v. Braun[1] compared the firmness of attachment of organic radicals to nitrogen atom by the reaction products of tertiary amines and cyanogen bromide; and K. v. Auwers[2] in his "quaternary indazolium salt method" by its thermal decomposition products.

As to the method to compare the "affinity requirement" of organic radicals to carbon atom Skraup and his co-workers proposed two methods, namely, "oxazol-[3]" and "carbinol method.[4]" In the former, the reaction velocity of ring rupture of substituted benzoxazoles is compared, and the latter is based on the assumption that basicity of various carbinols is due to the varying affinity of carbinol-carbon atom. Another method is given by Meerwein[5] during studies on pinacoline-rearrangement. As is well known, pinacone, when dehydrated, easily yields pinacoline by intramolecular rearrangement. The mechanism of this transformation was the subject of discussion over twenty-five years, but finally Tiffeneau[6] concluded that this rearrangement occurs together with elimination of water through a "fraction of a molecule,"  which cannot be isolated. Then in the

(1) *Ber.*, **55** (1922), 3165; **56** (1923), 1573. $R'R''R'''N + BrCN = R'R''N{\cdot}CN + R'''Br$.

(2) *Ber.*, **58** (1925), 1360. $[C_6H_4\langle^{CH}_{NR'}\rangle NR'']{\cdot}X \rightarrow C_6H_4\langle^{CH}_{NR'}\rangle N + R''X$ or $C_6H_4\langle^{CH}_{N}\rangle NR'' + R'X$.

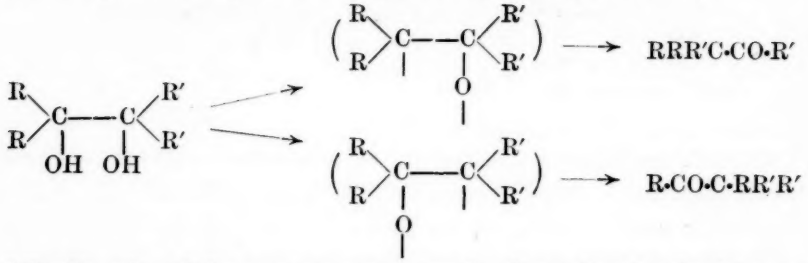
(3) *Ann.*, **419** (1919), 1; *Ber.*, **55** (1922), 1080. $C_6H_4\langle^{N}_{O}\rangle CR + H_2O \rightarrow C_6H_4\langle^{NHCOR}_{OH}$.

(4) *Ber.*, **55** (1922), 1074.

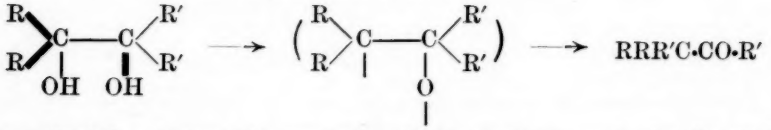
(5) *Ann.*, **419** (1919), 121.

(6) *Compt. rend.*, **143** (1906), 687.

case of unsymmetrically substituted pinacones, we may have:



and the direction of the rearrangement may be determined by the firmness of the union of the two hydroxyl radicals. Now, Meerwein considered that the carbon atom combined to hydrocarbon radicals which possess greater "affinity requirement" leaves less affinity to combine with hydroxyl group, consequently it is this hydroxyl radical which is removed on dehydration. The scheme of the rearrangement is as follows:

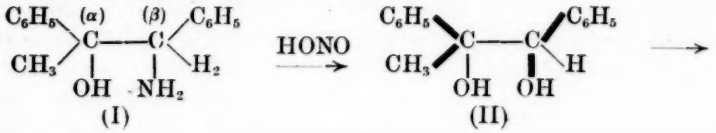


where thick bar denotes the greater "affinity requirement." By the studies on various pinacones he determined the relative "affinity requirement" of several radicals. In addition to his result, taking in consideration those given by Skraup,[1] we have the following series:

$C_6H_5{\cdot}CH_2- < C_2H_5- < CH_3- < C_6H_5- < p\text{-}CH_3{\cdot}C_6H_4- < p\text{-}CH_3O{\cdot}C_6H_4- < C_{10}H_7-$.

Action of nitrous acid on tertiary amino-alcohols. Few years ago Mc Kenzie[2] found that tertiary amino-alcohols, when acted by nitrous acid, do not give normally glycols but they perform a kind of pinacoline rearrangement which he proposed to call *semipinacolinic deamination*. Now, if we attempt to predict the result of this transformation by the theory of "affinity requirement" as in the case of pinacones, we will be surprised at unexpected results (see Table below).

For example, in the case of β-amino-α β-diphenyl-α-methyl-ethyl-alcohol (I), we expect the following course of reaction:

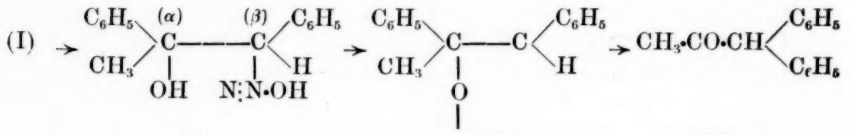


(1) Loc. cit.

(2) McKenzie and Richardson, *J. Chem. Soc.*, **123** (1923), 79.

(III) (IV)

The transformation from (III) to (IV) is explained thus: out of the two substituents attached to β-carbon atom the less firmly combined hydrogen atom migrates to α-carbon atom, giving phenyl-methyl-acetophenone (IV). But the product actually obtained is diphenyl-acetone $(C_6H_5)_2CH{\cdot}CO{\cdot}CH_3$. In order to explain this contradiction, McKenzie supposed that the transformation occurs in the following manner:



(V) (VI) (VII)

Owing to the easiness with which nitrogen is eliminated, the hydroxyl group attached to α-carbon atom is more firmly bound than is the nitrogen atom attached to β-carbon atom, so that the linkage $-N_2OH$ would be severed first. Though this assumption accounts for the mode of dehydration in all the semipinacolinic deamination of amino-alcohols, it can not explain why certain tertiary amino-alcohols such as γ-amino-$\alpha\alpha\gamma$-triphenyl-propyl alcohol,[1] $(C_6H_5)_2C(OH){\cdot}CH_2{\cdot}CH(NH_2){\cdot}C_6H_5$ and β-amino-β-phenyl-$\alpha\alpha$-diethyl-ethyl alcohol,[2] $(C_2H_5)_2C(OH){\cdot}CH(NH_2){\cdot}C_6H_5$ behave normally toward nitrous acid, giving corresponding glycols. Moreover, as the theory of "affinity requirement" can not explain why in the above example, phenyl group which is to be considered more firmly bound than methyl group migrates in the last stage of the reaction (VI)→(VII), we must admit the provision that a certain migrational aptitude is conceded to each radical, this property being not necessarily concomitant with its saturation capacity.[3] This means that the theory of "affinity requirement" can not foretell the products of semipinacolinic deamination of tertiary amino-alcohols, except those of the type $R_2C(OH){\cdot}CHR'(NH_2)$.

(1) McKenzie and Richardson, *J. Chem. Soc.*, **123** (1923), 85.
(2) Ibid., **1927**, 571.
(3) Tiffeneau and Lévy, *Compt. rend.*, **176** (1923), 312.

TABLE 1.

The Products of Semipinacolinic Deamination of Tertiary Amino-alcohols.

No.	Tert. amino-alcohol.	Actual product.	Product expected from	
			Electron theory	Affinity-requirement
1.	$Ph_2C(OH)\cdot CHPh(NH_2)$	$Ph_2CH\cdot CO\cdot Ph$	The same.	The same.
2.	$PhMeC(OH)\cdot CHPh(NH_2)$	$Ph_2CH\cdot CO\cdot Me$	The same.	The same.
3.	$PhEtC(OH)\cdot CHPh(NH_2)$	$Ph_2CH\cdot CO\cdot Et$	The same.	$PhEtCH\cdot CO\cdot Ph$
4.	$PhNapC(OH)\cdot CHPh(NH_2)$	$Ph_2CH\cdot CO\cdot Nap$	$PhNapCH\cdot CO\cdot Ph$	$PhNaCH\cdot CO\cdot Ph$
5.	$Ph_2C(OH)\cdot CHMe(NH_2)$	$PhMeCH\cdot CO\cdot Ph$	The same.	$Ph_2CH\cdot CO\cdot Me$
6	$Ph_2C(OH)\cdot CHBzl(NH_2)$	$PhBzlCH\cdot CO\cdot Ph$	The same.	$Ph_2CH\cdot CO\cdot Bzl$
7.	$Ph_2C(OH)\cdot CH_2(NH_2)$	$PhCH_2\cdot CO\cdot Ph$	The same.	$Ph_2CH\cdot CHO$
8.	$PhAnisC(OH)\cdot CH_2(NH_2)$	$AnisCH_2\cdot CO\cdot Ph$	The same.	$PhAnisCH\cdot CHO$
9.	$PhNapC(OH)\cdot CH_2(NH_2)$	$NapCH_2\cdot CO\cdot Ph$	The same.	$PhNapCH\cdot CHO$
10.	$Bzl_2C(OH)\cdot CHMe(NH_2)$	$BzlMeCH\cdot CO\cdot Bzl$	The same.	— *
11.	$Bzl_2C(OH)\cdot CHPh(NH_2)$	$BzlPhCH\cdot CO\cdot Bzl$	The same.	— *

Ph = Phenyl, Me = Methyl, Et = Ethyl, Nap = Naphthyl, Bzl = Benzyl, Anis = *p*-Anisyl.

* As the difference of the "affinity requirement" between two benzyl groups and hydrogen atom plus phenyl (or methyl) group is not known, we can say nothing about the products of the rearrangement in these cases.

Literatures.

1. McKenzie and Richardson, *J. Chem. Soc.*, **123** (1923), 79; McKenzie and Wills, ibid., **127** (1925), 283.
2. McKenzie and Richardson, loc. cit.; McKenzie and Roger, ibid., **125** (1924), 844.
3. McKenzie and Roger, ibid., **1927**, 574.
4. McKenzie and Dennler, ibid., **125** (1924), 2105; Orékhov and Tiffeneau, *Compt. rend.*, **178** (1924), 1619.
5 and 6. McKenzie and Wills, loc. cit.
7. Bettzieche, *Z. physiol.* **140** (1924), 273.
8. Orékhov and Tiffeneau, *Compt. rend.*, **180** (1925), 70.
9. Luce, ibid., 145.
10 and 11. Bettzieche and Ehrlich, *Z. physiol.*, **150** (1925), 197.
11. McKenzie and Roger (*J. Chem. Soc.*, **1927**, 574) obtained further the corresponding glycol as a by-product

Interpretation from the Electron Theory.

In order to deduce a more reliable theory which interprets without a provision all the rearrangements similar to pinacoline transformation, I have determined the standpoint of the interpretation in the modern electron theory which has been developed by Lapworth[1] and by Kermack and Robinson.[2] This theory has great possibility to explain clearly the

(1) *J. Chem. Soc.*, **121** (1922), 461.
(2) Ibid., 427.

mechanism of the most essential parts of these transformations, that is (i) elimination of water from a molecule, and (ii) migration of a group.

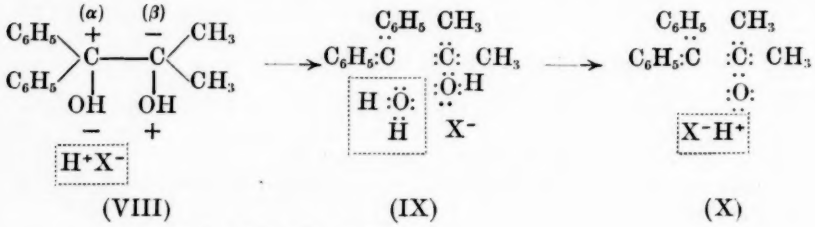
In the discussion of the mechanism of a reaction of organic compounds, especially of those which contain various hydrocarbon radicals as in our case, we must first determine the relative electro-negativity of these radicals. This question has already been solved by Kharasch and Marker,[1] from the studies of the reaction between unsymmetrical dialkylmercuric compounds and hydrogen chloride. The reaction runs as follows:

$$R.Hg.R' + HCl = RH + R'.HgCl,$$

where the relatively electro-negative radical combines with hydrogen atom. In this way the electro-negativity of hydrocarbon radicals are found to be α-$C_{10}H_7$-> p-$CH_3O \cdot C_6H_4$-> o,p-$CH_3 \cdot C_6H_4$-> C_6H_5-> CH_3-> C_2H_5-, C_3H_7-> $C_6H_5 \cdot CH_2$-[2]

1. The Mechanism of Pinacoline Rearrangement. From the fact that the pinacoline rearrangement occurs only in the presence of acid and that pinacone remains unchanged when boiled with soda-solution or when heated with water at 120°–130°, it may be assumed that *acid behaves in this case not only as dehydrating agent but also as a catalyst* as in the case of the rearrangement of phenyl-chlor-amine into p-chlor-aniline ($C_6H_5 \cdot NH \cdot Cl \rightarrow Cl \cdot C_6H_4 \cdot NH_2$). This assumtion may be considered probable since the rearrangement of tertiary amino-alcohols occurs in the presence of nitrous acid only, without ordinary dehydrating agent.

Then the mechanism of the rearrangement of unsym. diphenyl-pinacone may be formulated as follows:



(VIII) (IX) (X)

$\longrightarrow (C_6H_5)_2CH_3C \cdot CO \cdot OH_3$

(XI)

As α- and β-carbon atoms are induced respectively positive and negative, the former by the influence of phenyl and the latter by methyl group; the

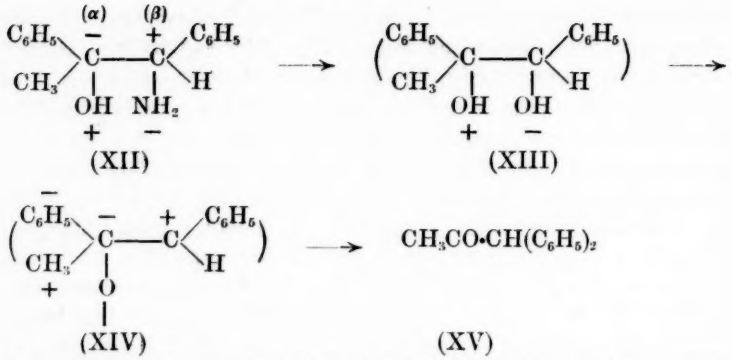
(1) *J. Am. Chem. Soc.*, 48 (1926), 3130.

(2) This result shows a good agreement with the order of "affinity requirement" given above. But this concordance is not merely accidental, as the electron theory involves in itself the principle of "affinity requirement."

theory of induced alternate polarity demands that hydroxyl group attached to α-carbon atom has negative polarity (VIII). Consequently it is this hydroxyl group that is attracted by hydrogen ion of the acid, when an acid H^+X^- is acted on this pinacone. This attraction weakens the linkage between this hydroxyl group and α-carbon atom and increases the positive character of this carbon atom. In other words, the octet around this carbon atom becomes more and more unstable, and this causes, on the other hand, the increase of the stability of the octet of the adjacent carbon atom(β) (IX). As the results of this, hydrogen atom of the hydroxyl group bound to this negative carbon atom (β) will be brought into very free state and can combine with anion X^- of the acid (X). Then the disturbance of the distribution of electrons is restored by the migration of one of the methyl groups to α-carbon atom and by sharing four electrons between β-carbon- and oxygen atoms (XI). This final product is the same as that derived by Meerwein from the theory of "affinity requirement." The rearrangement of pinacones, $R_2C(OH).CR'_2(OH)$, where R and R′ are alkyl or aryl radicals, can be likewise interpreted. When the polarity difference between the two carbon atoms (α and β) is not marked, as is in the cases of pinacones with different R and R′, the homologous aliphatic radicals, the rearrangement takes its course in two directions, giving two isomeric ketones in different quantities, where the proportion of the two ketones formed is dependent on the polarity difference between the α- and β-carbon atoms.

2. The Mechanism of Semipinacolinic Deamination of Tertiary Amimo-alcohols. Now taking again β-amino-$\alpha\beta$-diphenyl-α-methyl-ethyl alcohol as an example, the "key stom" which causes the polarity in this molecule, when placed in an activated state, may be assumed to be the most negative and reactive amino group. In consequence of the induced alternate polarity caused by this negative key atom, β-carbon atom is induced strongly positive, α-carbon atom negative and the hydroxyl group positive in its turn (XII). Then the corresponding glycol, which is assumed to be formed when amino-alcohol is treated with nitrous acid, will have strongly negative hydroxyl group bound to β-carbon atom (XIII), therefore, according to the mechanism described in the last section, it must give such a "fraction of molecule" as (XIV). Further, if one of the group attached to α-carbon atom migrates to β-carbon atom in order to restore the disturbance of the affinity, the group that wanders must be the one that is more negative, since β-carbon atom has positive polarity. Thus in this case it is the phenyl group that wanders, and the final product must be diphenyl acetone (XV). This interpretation is proved by the actual product of the rearrangement.

(1) Vorländer, *Ber.*, **30** (1897), 2766.



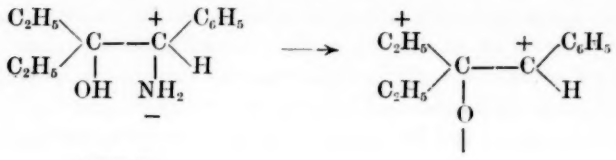
(XII) (XIII)

(XIV) (XV)

It is obvious from Table 1 that this interpretation in the prediction of the product of the semipinacolinic deamination is not only applicable in this one example, but also gives satisfactory results in many other cases. Out of a dozen examples the case which stands against this interpretation is only one, that is, that of β-amino-α β-diphenyl-α-naphthyl-ethyl alcohol (No. 4 in the Table) in which phenyl group which is more positive than naphthyl group wanders to β-carbon atom. This might be considered due to some steric influence of the phenyl group attached to β-carbon atom, since in the case of the β-amino-α phenyl-α-naphthyl-ethyl alcohol (No. 9) the rearrangement takes the normal course.

3. Behaviour of Tertiary Amino-Alcohols towards Nitrous Acid. The electronic interpretation can explain why tertiary amino-alcohols generally undergo semipinacolinic deamination by nitrous acid, whereas in few cases normal displacement of amino group takes place. In the former, the state of marked polarity developed in the molecule due to the presence of a strongly negative group such as amino radical may be sufficient to cause the molecular transformation by mere catalytic action of the acid present. This may account at the same time, for the normal displacement of amino group in the cases of γ-amino-$\alpha\alpha\gamma$-triphenyl-propyl alcohol (XVI) and of β-amino-β-phenyl-$\alpha\alpha$-diethyl-ethyl alcohol (XVII). Because in the former, the fact that two hydroxyl groups in the corresponding glycol are induced in the same sence, may be considered to play an important rôle, and in the latter, the ethyl group cannot easily migrate to the positively polarised β-carbon atom in consequence of its positive character.

(XVI)



(XVII)

4. The Rearrangements of Trisubstituted α-Glycols. Which afford an interesting problem by the variety of their modes of transformation, will be discussed in another paper.

Conclusion.

Hitherto the rearrangements of pinacones and their closely related compounds have been interpreted from the theory of "affinity requirement." But as this theory is compelled to admit the provision that the migrational aptitude of a certain group is not necessarily concordant with its "affinity requirement," it cannot generally foretell the rearrangement product.

An interpretation based on the theory of induced alternate polarity and on the assumption that acid behaves in these rearrangements not only as dehydrating agent but also as a catalyst, has following advantages:

(1) The products of rearrangements of pinacones and tertiary amino-alcohols are reliably predicted by one and the same reasoning.

(2) We can also explain why tertiary amino-alcohols generally behave abnormally toward nitrous acid, whereas in certain cases normal displacement of amino group takes place.

Of course, this electronic interpretation is by no means perfect, on the contrary, there remains a fundamental problem undissolved. That is a question of the steric influence. The steric influence is an important, but an unknown factor, which, as well as the general and alternate effects due to a key atom, has a directive influence on a chemical reaction. It must be the most important task given on the electron theory to bring the nature of this influence to light. Besides this fundamental problem, the above electronic interpretation has some contradictory facts:

(1) The rearrangements of alkyl-trimethyl pinacones propose a strong objection to this interpretation, for they give ketones, $CH_3 \cdot CO \cdot CR(CH_3)_2$, by the migration of the more positive group.[1]

(2) When β-amino-β-phenyl-$\alpha\alpha$-diethyl-ethyl alcohol is treated with nitrous acid, the main product is the corresponding glycol, as already

(1) R=C_2H_5, Meerwein, *Ann.*, **396** (1896), 255; R=n- and iso-C_3H_7, Locquin and Leers, *Bull. Soc. chim.*, **39** (1926), 426.

described, while according to the above explanation in the case of β-amino-β-phenyl-αα-dibenzyl-ethyl alcohol the normal displacement of amino group should take place at least as easily as in the former case, since as benzyl is more positive than ethyl, it should migrate more difficultly to positively polarized β-carbon atom. But the actual products betray this prediction, for it gives the glycol only as a by-product.(1)

These contradictions will be discussed again when a sufficient number of new experimental materials are obtained.

I with to express my hearty thanks to Prof. K. Matsubara for his kind inspection of this paper.

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SYNTHESIS OF THE ESTERS OF β-BENZYL-α,γ-DICYANOGLUTACONIC ACID.

By **Yoshiyuki URUSHIBARA.**

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The formation of the sodium derivative of diethyl β-methyl-α, γ-dicyano-glutaconate $C_2H_5OCO(CN)C{:}C(CH_3){\cdot}CNa(CN)COOC_2H_5$ in the condensation of ethyl ethoxy-ethylidene-cyanoacetate $C_2H_5OC(CH_3){:}C(CN)COOC_2H_5$ with ethyl sodio-cyanoacetate $CHNa(CN)COOC_2H_5$ let the author suppose that any compound with the general formula $C_2H_5OCR : C(CN)COOC_2H_5$ will condense with ethyl sodio-cyanoacetate, yielding the following product:

$$C_2H_5OCO(CN)C{:}CR{\cdot}CNa(CN)COOC_2H_5.$$(2)

Subsequently the author carried out experiments on the synthesis of the esters of β-benzyl-α, γ-dicyanoglutaconic acid,

$$ROCO(CN)C : C(CH_2C_6H_5) \cdot CH(CN)COOR.$$

Diethyl β-Benzyl-α,γ-dicyanoglutaconate. The sodium derivative of this ester, $C_2H_5OCO(CN)C : C(CH_2C_6H_5) \cdot CNa(CN)COOC_2H_5$, must be given by the condensation of ethyl α-cyano-β-ethoxy-γ-phenyl-crotonate $C_2H_5OC(CH_2C_6H_5) : C(CN)COOC_2H_5$ and ethyl sodio-cyanoacetate. Ethyl α-cyano-β-ethoxy-γ-phenyl-crotonate has been already obtained by Smith and

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(1) McKenzie and Roger, *J. Chem. Soc.*, 1927, 574.
(2) See p. 102 and 261 of this volume.

Thorpe.[1] It seems difficult to obtain a sufficient amount of this compound in the pure crystalline state, for these authors describe that the ethylation product of the silver derivative of ethyl α-cyano-γ-phenyl-acetoacetate was a mixture of two isomerides, ethyl α-cyano-β-ethoxy-γ-phenyl-crotonate and ethyl α-cyano-α-ethyl-γ-phenyl-acetoacetate, which could not be separated by distillation. The present author gave up the idea to obtain the pure ethyl α-cyano-β-ethoxy-γ-phenyl-crotonate, and used it without separating from its isomeride.

The method of preparation of ethyl α-cyano-γ-phenyl-acetoacetate was improved as follows: Powdered sodium (2 atoms) was covered with a large amount of pure benzene and an excess of ethyl cyanoacetate (over 2 mols) was introduced gradually. On several hours' standing, the mixture was converted into a white thick paste. Phenacetyl chloride (1 mol) was then added in small portions under constant stirring and cooling. The mixture was heated on the water bath for a while, and cooled. The sodium derivative of ethyl α-cyano-γ-phenyl-acetoacetate formed in this way was extracted with water. The aqueous solution was acidified with dilute sulphuric acid and the oily substance was extracted with ether. After dehydrating the ethereal solution with calcium chloride and evaporating away the ether, the ester was distilled under diminished pressure. Ethyl α-cyano-γ-phenyl-acetoacetate was transformed into the silver derivative by dissolving it in an aqueous solution of the calculated amount of sodium hydroxide and adding to this solution the calculated amount of a silver nitrate solution. The silver compound was washed with water and completely dried in vacuum in a dark place.

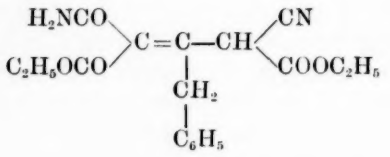
A mixture of the dried silver compound, an excess of ethyl iodide, and absolute alcohol, was boiled for a while with a reflux condenser. The alcoholic solution was filtered from silver iodide and evaporated. The residue was dissolved in ether and the ethereal solution was shaken with an aqueous solution of sodium carbonate until the latter remained alkaline. Then it was washed with water, dried with calcium chloride and evaporated. The ether was removed in vacuum over sulphuric acid as much as possible. The oily substance obtained in this way and containing ethyl α-cyano-β-ethoxy-γ-phenyl-crotonate was used for the condensation without further treatments.

Sodium (1 gram atom) was dissolved in absolute ethyl alcohol and ethyl cyanoacetate (1 mol) was added. Then ethyl α-cyano-β-ethoxy-γ-phenyl-crotonate (1 mol) was introduced, the above-described oily substance being assumed to consist of this compound alone. The alcoholic solution was evaporated to dryness in vacuum, and the residue was dissolved in water.

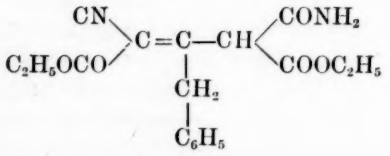
(1) *J. Chem. Soc.*, 91 (1907), 1905.

The insoluble oily substance might be the ethyl α-cyano-α-ethyl-γ-phenyl-acetoacetate which was indifferent in the reaction. This was removed by shaking the aqueous solution with ether. On adding dilute hydrochloric acid to the aqueous solution an oily substance separated out, which was extracted with ether. Some amount of the sodium derivative of ethyl cyanoacetate might be left intact, for the ethyl α-cyano-β-ethoxy-γ-phenyl-crotonate had contained its isomeride indifferent in the reaction. On dissolving the condensation product in water, the ethyl sodio-cyanoacetate is at once transformed into sodium cyanoacetate and alcohol. Therefore, on acidifying the aqueous solution the ethyl cyanoacetate was not to be regenerated, and this fact facilitated the subsequent treatment.

The ethereal solution was washed with water. After a while, colourless crystals began to separate from the ethereal solution not yet dried. When the increase of the crystals ceased, they were collected, washed with ether and then with water. This crystalline substance was recrystallised from alcohol. It melted at 131°. By analysis it was found to be diethyl β-benzyl-cyano-carbamyl-glutaconate, and not the diethyl β-benzyl-α,γ-dicyanoglutaconate. 0.1943, 0.2022 Gr. of the substance gave 0.4465, 0.4622 gr. of CO_2 and 0.1001, 0.1044 gr. of H_2O respectively; 0.2462, 0.2727 gr. of the substance gave 18.3 c.c. (26.5°, 759.5 mm.), 20.15 c.c. (26.5°, 761. 9 mm.) of nitrogen respectively. (Found: C=62.69, 62.36; H=5.77, 5.78; N=8.18, 8.15. $C_{18}H_{20}O_5N_2$ requires C=62.75; H=5.86; N=8.14%.) On heating at about 90° or dehydrating in vacuum, it lost no water. This compound must be either of the following:



diethyl β-benzyl-α-cyano-α-carbamyl-glutaconate;



diethyl β-benzyl-γ-cyano-α-carbamyl-glutaconate.

The oily substance which was afterwards changed in the crystalline monohydrate must be diethyl β-benzyl-α,γ-dicyanoglutaconate, $C_2H_5OCO(CN)C:C(CH_2C_6H_5)\cdot CH(CN)COOC_2H_5$. Inspite of the impureness

of the ethyl α-cyano-β-ethoxy-γ-phenyl-crotonate the condensation proceeded successfully as follows:

$$NaOC_2H_5 + CNCH_2COOC_2H_5 + C_2H_5OC(CH_2C_6H_5) : C(CN)COOC_2H_5$$
$$= C_2H_5OCO(CN)C : C(CH_2C_6H_5)\cdot CNa(CN)COOC_2H_5 + 2\ C_2H_5OH.$$

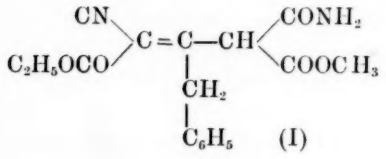
Although the sodium compound was not isolated, it was contained in the aqueous solution of the condensation product and it gave the free cyano-ester on acidifying, and the latter was then transformed into the monohydrate in the ethereal solution.

Methyl Ethyl Esters. Following the similar procedure the author carried out the experiment on the condensation of ethyl α-cyano-β-ethoxy-γ-phenyl-crotonate with methyl cyanoacetate in the presence of sodium methylate. The final product was the monohydrate of methyl ethyl β-benzyl-α, γ-dicyanoglutaconate melting at about 115°. 0.1930 Gr. of the substance gave 0.4351 gr. of CO_2 and 0.0946 gr. of H_2O; 0.2547 gr. of the substance gave 19.3c.c. of nitrogen at 22.5°, 761.8 mm. (Found: C = 61.50; H = 5.49; N = 8.54. $C_{17}H_{18}O_5N_2$ requires C = 61.79; H = 5.50; N = 8.48 %.) (Specimen A)

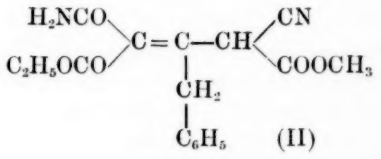
The condensation must be represented by the following equation:

$$C_2H_5OCO(CN)C{:}C(CH_2C_6H_5)OC_2H_5 + CH_2(CN)COOCH_3 + NaOCH_3$$
$$= C_2H_5OCO(CN)C : C(CH_2C_6H_5)\ CNa(CN)COOCH_3 + CH_3OH + C_2H_5OH.$$

The monohydrate $C_{17}H_{18}O_5N_2$, in which the sodium atom is replaced by hydrogen and either of the two cyano-groups is hydrated into a carbamyl-group, must be represented by either of the following formulas:



(I)



(II)

By starting from methyl α-cyano-β-ethoxy-γ-phenyl-crotonate[1], ethyl cyanoacetate, and sodium ethylate, another specimen of methyl ethyl β-benzyl-cyano-carbamyl-glutaconate was obtained. It melted at about 115°.

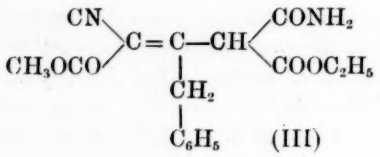
(1) This compound was prepared by a similar method as the ethyl ester. The sodium derivative of methyl cyanoacetate formed in benzene covered so compactly the surface of sodium grains that the transformation of methyl cyanoacetate into its sodium derivative was completed only by using a large excess of powdered sodium (about twice as much as necessary) and rubbing mechanically the sodium grains. On adding phenacetyl chloride and standing over night the metallic sodium disappeared. Then the mixture was worked on similarly as in the case of the ethyl ester. Methyl α-cyano-γ-phenyl-acetoacetate is a crystalline substance. This ester was transformed into methyl α-cyano-β-ethoxy-γ-phenyl-crotonate, which was used also without separating from its possible isomeride.

0.1889 Gr. of the substance gave 0.4261 gr. of CO_2 and 0.0928 gr. of H_2O 0.2501 gr. of the substance gave 18.9 c.c. of nitrogen at 23°, 760.7 mm. (Found: C=61.54; H=5.50; N=8.48. $C_{17}H_{18}O_5N_2$ requires C=61.79; H=5.50; N=8.48 %.) (Specimen B)

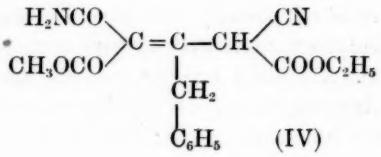
The condensation must be represented by the following equation:

$$CH_3OCO(CN)C:C(CH_2C_6H_5)OC_2H_5 + CH_2(CN)COOC_2H_5 + NaOC_2H_5$$
$$= CH_3OCO(CN)C:C(CH_2C_6H_5)\cdot CNa(CN)COOC_2H_5 + 2C_2H_5OH,$$

and the monohydrate by either of the following:



(III)



(IV)

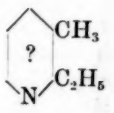
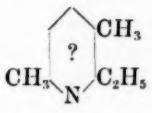
The four formulas, (I), (II), (III), and (IV), are different from one another, and, therefore, the two specimens, A and B, must be different; but according to the example of the β-methyl compounds[1], they may be expected to be identical. Really the mixture of the two specimens showed no depression of the melting point, but both the pure specimens and the mixture did not melt sharply. Each of the specimens A and B is not the direct product of the condensation but the compound derived from it by a secondary change which can admit two formulas for it, for instance, (I) and (II). These specimens must be, therefore, examined in their purity. Besides, the greatest care must be exercised with regards to the identification of them, because, if they are not identical, they have a great resemblance in the constitutions. For the present the author will reserve the conclusion that the specimens A and B are identical.

The auther expresses his hearty thanks to Prof. K. Matsubara for his kind inspection of this paper.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.

(1) See p. 261 of this volume.

CORRECTIONS TO VOLUME 3.

Page	Line	for	read
67	4	−0.1853	−0.1155
104	11	page 103	page 102
183	28	geletine	gelatine
191	18	suppercooled	supercooled
198	30	a_2NCO_3	Na_2CO_3
202	1	spitted	splitted
202	15	fomula	formula
203	foot-note	(1907)	(1887)
,,	,,	Inyold	Ingold
224	foot-note	(2)	(1)
230	22	247°	237°
231	29	nicotinic	dinicotinic
237	18	$d_4^{25} = 0.9229$	$d_4^{25} = 0.9299$
238	16	trimestic	trimesitic
239	30	quinolinite	quinolinate
242	Table, 6th column	0.9229	0.9299
,,	Table, 10th column		

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